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Progress towards a PETN Lifetime Prediction Model

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Disclaimer

Progress towards a PETN Lifetime Prediction Model[*]

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Dinegar (1) showed that decreases in PETN surface area causes EBW detonator function times to increase. Thermal aging causes PETN to agglomerate, shrink, and densify indicating a "sintering" process. It has long been a concern that the formation of a gap between the PETN and the bridgewire may lead to EBW detonator failure. These concerns have led us to develop a model to predict the rate of coarsening that occurs with age for thermally driven PETN powder (50% TMD).

To understand PETN contributions to detonator aging we need three things:

1. Curves describing function time dependence on specific surface area, density, and gap.
2. A measurement of the critical gap distance for no fire as a function of density and surface area for various wire configurations.
3. A model describing how specific surface area, density and gap change with time and temperature.

We've had good success modeling high temperature surface area reduction and function time increase using a phenomenological deceleratory kinetic model based on a distribution of parallel nth-order reactions having evenly spaced activation energies where weighing factors of the reactions follows a Gaussian distribution about the reaction with the mean activation energy (Figure 1). Unfortunately, the mean activation energy derived from this approach is high (typically ~75 kcal/mol) so that negligible sintering is predicted for temperatures below 40 $^{\circ}$C.

To make more reliable predictions, we've established a three-part effort to understand PETN mobility. First, we've measured the rates of step movement and pit nucleation as a function of temperature from 30 to 50 $^{\circ}$C for single crystals. Second, we've measured the evaporation rate from single crystals and powders from 105 to 135 $^{\circ}$C to obtain an activation energy for evaporation. Third, we've pursued mechanistic kinetic modeling of surface mobility, evaporation, and ripening.

The molar flux (J) away from a surface in presence of a foreign gas is given by $J = (pD)/zRT$, where p is the vapor pressure, D is the mutual diffusion constant for the molecule of interest in the foreign gas, and z is the distance from the evaporating surface where the partial pressure of the evaporating gas drops to zero. Consequently, one would expect the activation energy of evaporation to be close to the enthalpy of evaporation. In fact, that is what is observed. The measured activation energy of 35.2 kcal/mol is similar to the enthalpy of evaporation by several earlier workers.

A possible explanation for the substantial range in apparent activation energies comes from atomic force microscopy (AFM) measurements of PETN surface reconstruction as a function of time and temperature. An Arrhenius plot of step velocities vs temperature gives an activation energy of ~35 kcal/mol for both island shrinkage and pit growth, which is equal to the

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enthalpy and activation energies of evaporation. In contrast, and Arrhenius plot of nucleation frequency vs temperature gives an activation energy for pit nucleation is ~70 kcal/mol.

In parallel, a molecular forcefield was developed that matches crystal energies and structure. Kinetic Monte Carlo calculations using this forcefield have shown that some differences in crystal shape (asymmetry) can be attributed to the statistical nature of the growth process while others (length to width) are related to the probability of diffusion, which scales as temperature. One example of such a calculation is shown in Figure 4. Of particular interest is the energy for removal of a molecule from a kink in a molecular step on the crystal surface is approximately equal to the measured activation energy for step movement, and the energy for removal of a molecule from a smooth crystal face is approximately equal to the measured activation energy for nucleation. We are in the process of using the detailed modeling to formulate and calibrate more engineering-oriented sintering models.

In parallel, we are measuring and modeling the effects of changes in powder characteristics on detonator function time. Figure 5 shows a design for measuring the effect of gaps on the functioning of bridgewire and bridge foil detonators. Two PETN powders with surface areas of ~5000 and 6500 cm^2/g have been pressed to densities of 0.93 and 0.99 g/cm^3. A shim is then used to withdraw the pressed powder 2, 4, and 6 mils from the header. Experiments are currently in progress. Meanwhile, preliminary modeling has shown that gaps lead to a decrease in pressure generated at the PETN surface by the exploding bridgefoil (Figure 6).
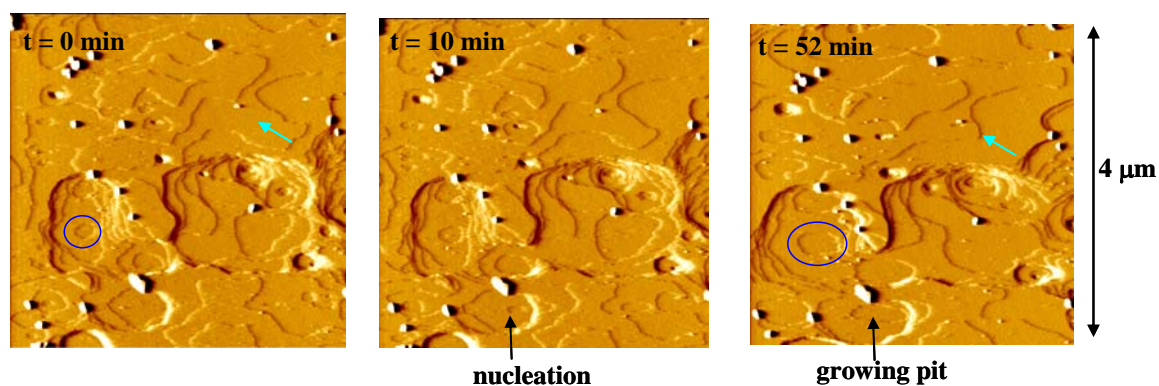
1. R. H. Dinegar, The effect of heat on pentaerythritol tetranitrate (P.E.T.N.), G.T.P.S. 105-107 (1987).
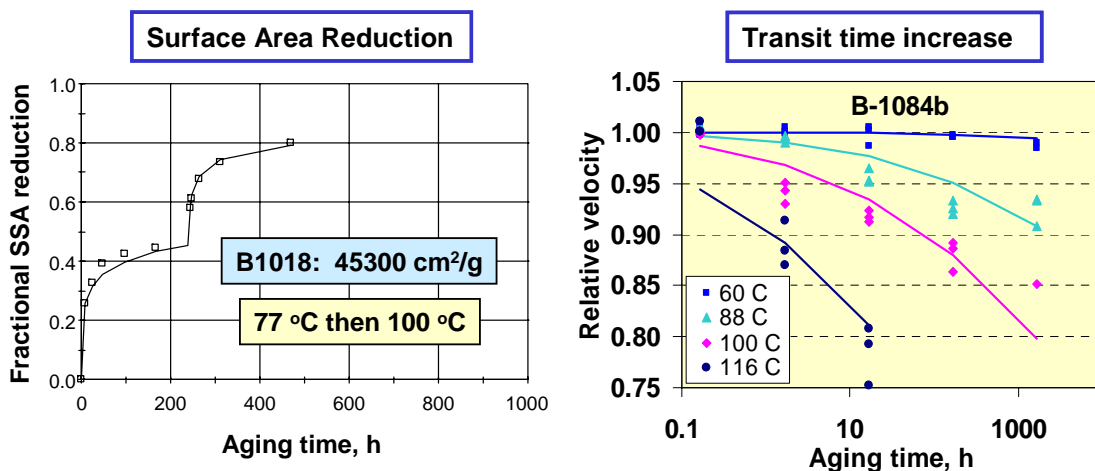

Figure 1. Model calculations of surface area reduction and function time increases using an nth-order Gaussian distribution reaction model.
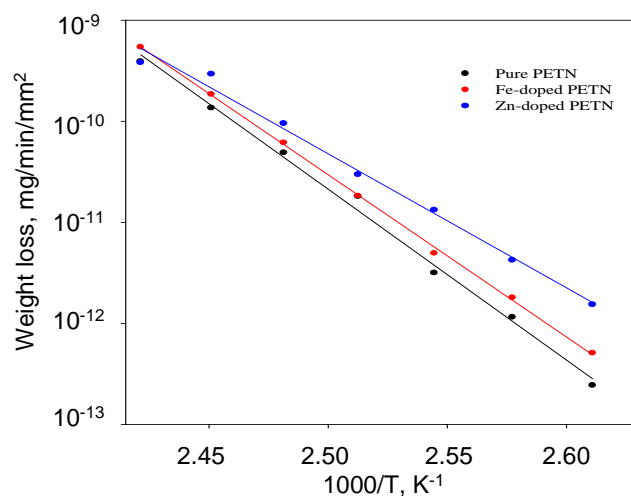
Figure 2. Arrhenius plot for the evaporation rate of pure and cation-doped PETN. Pure PETN has an activation energy of 35.2 kcal/mol.


Figure 3. AFM images as a function of time at a temperature of 30 ^{o}C. The turquoise arrow shows the recession of a molecular edge, and the blue circle shows the expansion of a pit. The black arrow points to a newly nucleated pit.
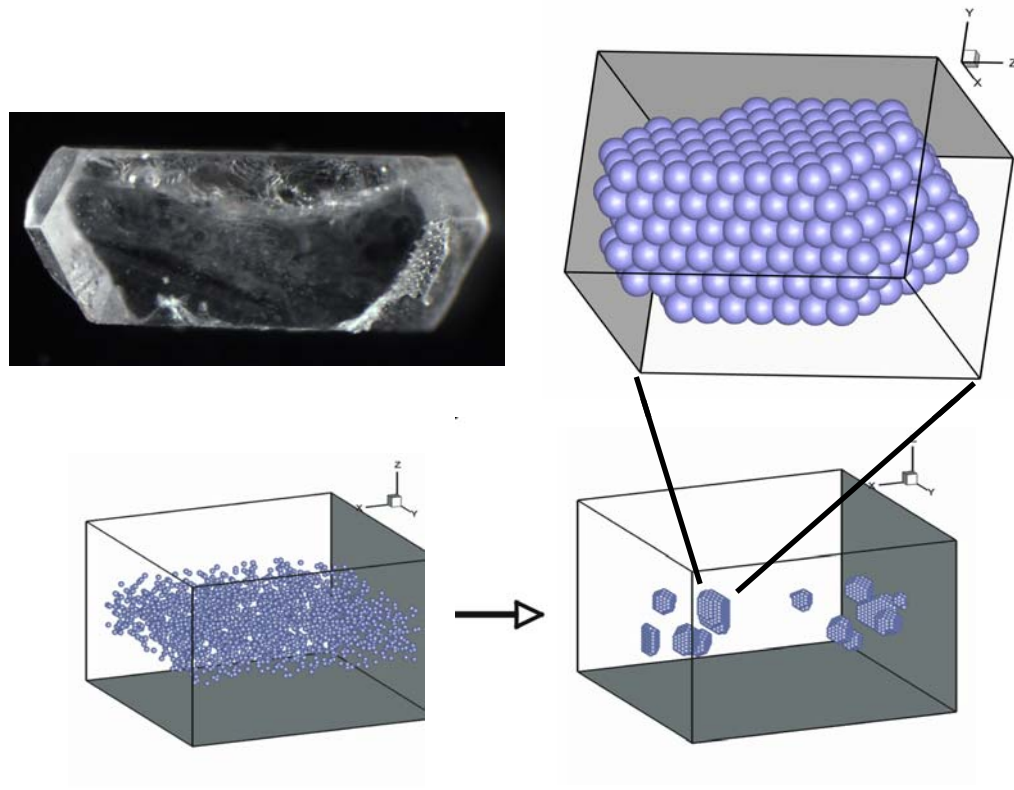
Figure 4. Simulation of a growing crystal by Kinetic Monte Carlo modeling, which yields a shape similar to that observed for well-formed PETN crystals.
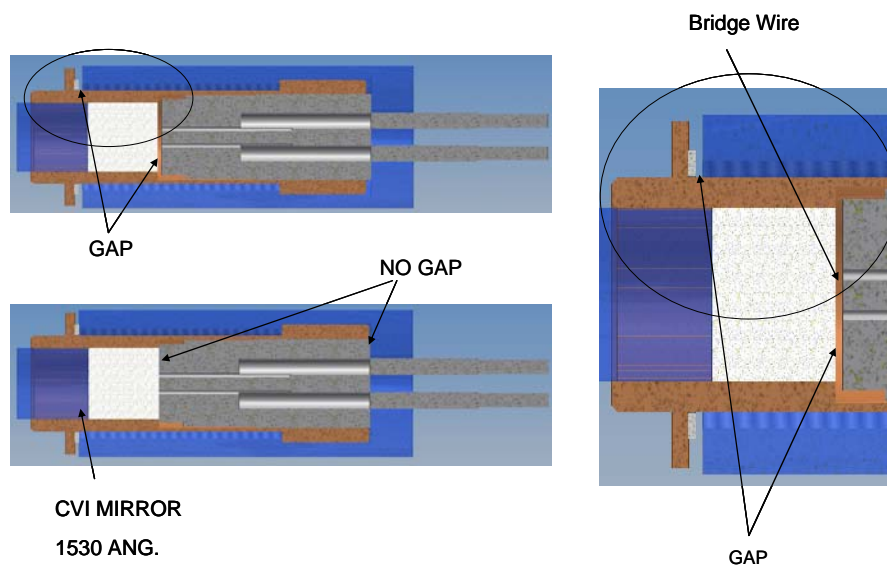
Figure 5. Design for measuring the effects of surface area, density, and bridgewire-PETN gap on detonator performance.
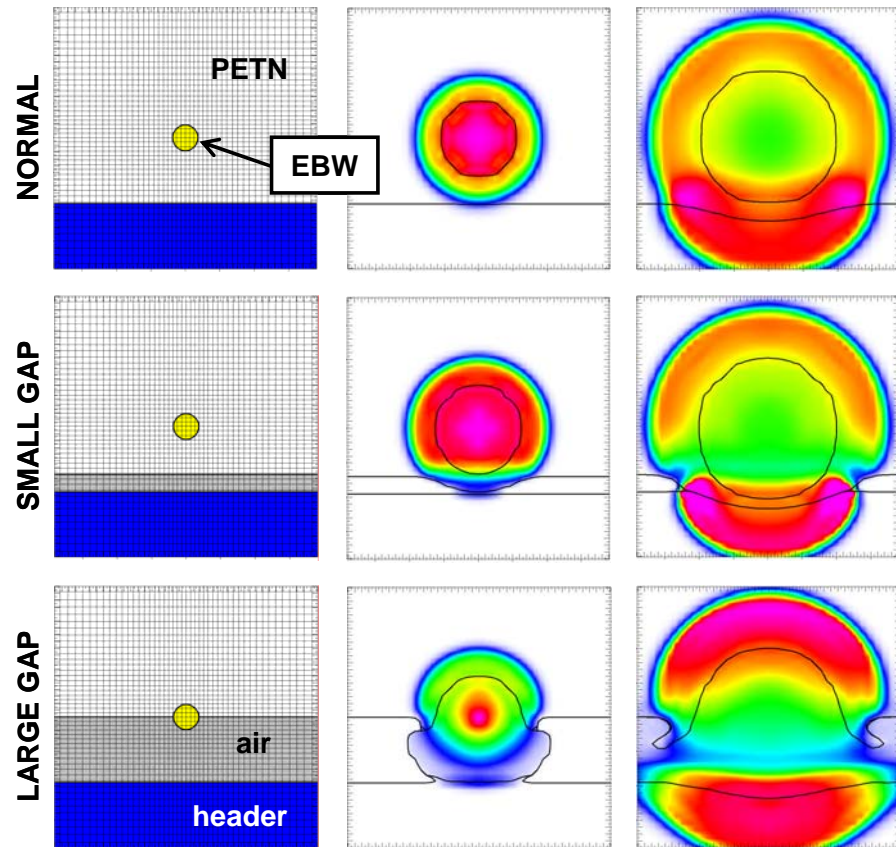
Pressure felt by PETN (pink high, blue low)

Figure 6. CALE calculations showing the effect of gaps on PETN detonator initiability. The color scale for any particular figure is pink high and blue low, but the colors are not on the same absolute scale for different figures. Gap formation due to densification of PETN during aging affects initiation by providing an escape route for the expanding exploding bridgewire. The peak pressure is 25% lower when the gap is present.